does not include the effect of impurities. The previously reported value is lower than the foregoing value by 0.16%, which difference is in excellent accord with the calculation based on 5.3 mole per cent. of styrene as impurity. In the new value, the uncertainty should be increased to ±0.30 kcal./mole to allow for the effect of impurities.

On the basis of the new value for the heat of combustion, the following values are calculated for the heat of formation and the heat of isomerization

8C(solid, graphite) + $4H_2$(gas) = C_8H_8(liquid, cyclooctatetraene); $\Delta Hf°_{298.16} = +60.82 \pm 0.32$ kcal./mole

1,3,5,7-cycloöctatetraene(liquid) = styrene(liquid); $\Delta H°_{298.16} = -36.10 \pm 0.36$ kcal./mole

The previous conclusion regarding the instability of the cycloöctatetraene ring, relative to the benzene ring, is unchanged.

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Anomalous Activation Energy in the Alkaline Hydrolysis of an Ether-ester[1]

BY BERNARD RABINOVITCH[*] AND CHARLES H. SCHRAMM

In the course of a study of the alkaline hydrolysis of swollen cellulose acetates, it became necessary to study the rates and activation energies of the alkaline hydrolysis of a series of simple esters. The purpose of this was to determine what effect, if any, a given group would have on the course of hydrolysis of an acetate group on a neighboring carbon atom. In this way we hoped to see how the state of substitution of a cellulose acetate chain might be expected to influence the rate of hydrolysis of its component ester groups.

Experimental

All the experiments were carried out at three temperatures between 15 and 25°. The hydrolyzing medium was a 50/50 volume/volume 0.1 *N* standard sodium hydroxide solution–acetone mixture, and the kinetics of the reactions were followed conductometrically.[2]

All the esters used were redistilled commercial products, none of which contained free acid. In all cases, any likely impurity could not affect the course of the reaction, and initial concentrations were always calculated from the OH^- ion concentration in the reaction mixture at the completion of the reaction.

Table I summarizes the results of these experiments for all except glycol diacetate, and this last-named behaves in exactly the same way (rate and activation energy) as glycol monoacetate, when ester concentration is expressed in terms of moles of acetate groups per liter (*cf.* Meyer's equation[3]).

The esters fall into a series: isopropyl, ethyl, 2-ethoxyethanol-1 and glycol acetates with increasing velocity constants

TABLE I

Ester	Velocity constant[a] (mole⁻¹ min.⁻¹ liters) 15°	20°	25°
Isopropyl acetate	0.335	0.49	0.68
Ethyl acetate	1.79	2.53	3.67
2-Ethoxyethanol-1 acetate	3.56	5.75	8.83
Glycol monoacetate	7.37	10.52	14.12

[a] Estimated error ±1%.

However, when activation energies are considered, a discrepancy shows up (see Fig. 1). In all cases but one, the energy of activation is 11,700 ± 300 cal./mole but 2-ethoxyethanol-1 acetate (ethyl cellosolve acetate) gives a value of 15,400 ± 300 cal./mole.

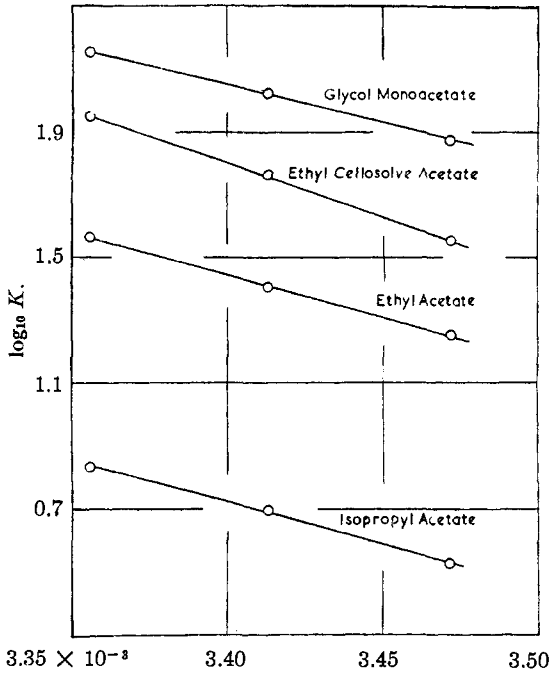

Fig. 1.—Activation energies of series of esters.

Discussion.—The increasing velocity constants of alkaline hydrolysis in this series of esters is to be expected on account of the increasing basic strength; $(CH_3)_2CH$–, C_2H_5–, $C_2H_5OC_2H_4$– and HOC_2H_4–. At the same time, for a reaction in solution between a dipolar molecule and an ion, a constant value for the energy of activation in such a series is not surprising.[4]

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[*] Harvard University, Eli Lilly Research Fellow, 1948–1949.

(1) From work done at the Department of Colloid Science, University of Cambridge, England.

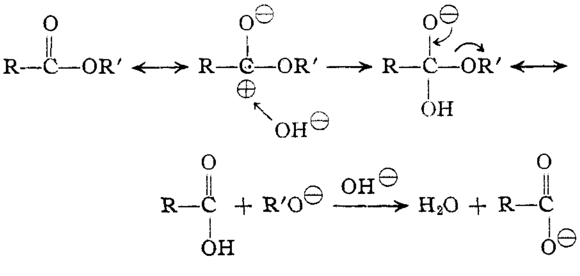
(2) Rabinovitch and Alexander, THIS JOURNAL, 72, 293 (1950).

(3) J. Meyer, *Z. physik. Chem.*, 67, 257 (1909).

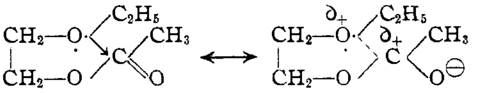
(4) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, 1947, p. 124.

That 2-ethoxyethanol-1 acetate should deviate from this regularity indicates that a factor, not present in the other members of the series, has been introduced and which affects the ease of the reaction.

An explanation for this discrepancy can be found in the commonly accepted mechanism for the basic hydrolysis of esters.



Now, in the case of the ether ester, the ether-oxygen atom can partially donate its unpaired electrons to the carbon atom at which the attack is to be made by the hydroxyl ion, thereby forming a "quasi" five-membered ring



Ingold and Nathan[5] have found that, in the case of para-substituted benzoic esters, groups which donate electrons to the site of attack will increase the energy of activation of the reaction. It would appear that this effect is operating in the case of the "quasi" five-membered ring, while the existence of steric hindrance due to the ethoxy group cannot be excluded. In addition to a raising of the energy of activation, one would expect a slowing down of the reaction, but this cannot be shown from the above data, although there is no reason for suspecting that this has not been the case.

It is of interest to compare these conclusions with those drawn by T. I. Crowell and L. P. Hammett from their work on the reaction of the thiosulfate ion on alkyl bromides.[6] The decrease in rate of reaction in going from ethyl to isopropyl bromide is attributed to an increase in the activation energy of the latter reaction, whilst in going from ethyl to propyl bromide the decreased rate is attributed to a decrease in the entropy of activation. It would seem that our series would conform with this latter case, since the increase in rates in the series must, it seems, be due to increases in entropy of activation, with an especially large jump from the ethyl to the ether-ester.

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[5] Ingold and Nathan, *J. Chem. Soc.*, 222 (1936).

[6] T. I. Crowell and L. P. Hammett, THIS JOURNAL, **70**, 3444 (1948).

The σ-Constants of the Cyano Group

BY JOHN D. ROBERTS* AND ELIZABETH A. MCELHILL

Despite the importance of the cyano group as a substituent group of organic compounds, relatively few data are available for the quantitative evaluation of its electrical effect on organic reactions. Thus, while Hammett's compilation[1] includes a value (based on a single reaction) for the σ-(substituent) constant of the *m*-cyano group, none is given which applies to compounds other than anilines or phenols for the *p*-cyano group.

As part of another investigation we have had occasion to determine the influence of the *m*- and *p*-cyano groups on the reactivity of benzoic acid and, hence, the corresponding σ-constants. The reactions and procedures have been described previously in detail.[2] The apparent ionization constants at 25° in 50% water–50% ethyl alcohol (by volume) of *m*- and *p*-cyanobenzoic acids[3] were 1.41×10^{-5} and 2.00×10^{-5}, respectively, while the corresponding rate constants (k_2) for the acids with diphenyldiazomethane at 30° in absolute ethyl alcohol were 4.55 and 4.22 l./mole-min. The σ-constants calculated from all of the data now available are given in Table I. The average value of σ for the *p*-cyano group is +0.656 with a median deviation, *r*, of 0.034. The corresponding values for the *m*-cyano group are +0.608 and 0.054, respectively.

TABLE I

σ-CONSTANTS OF CYANO GROUP

Reaction	Log k_0	ρ	σ-*para*	σ-*meta*
Phenylate ions with oxiranes, 98% ethyl alcohol, 70.4°[a]	−4.254	−0.946	......[b]	+0.678
Ionization of benzoic acids, water, 25°[a]	−4.203	+1.000	+0.651[c]	+ .520[c]
Ionization of benzoic acids, 50% ethyl alcohol, 25°[d]	−5.71	+1.464	+ .695	+ .590
Benzoic acids with diphenyldiazomethane, 100% ethyl alcohol, 30°[d]	+0.041	+0.937	+ .622	+ .645

[a] Ref. 1. [b] The value obtained from this reaction is only applicable to anilines and phenols. [c] Calculated from the data of Kilpatrick and Eanes, THIS JOURNAL, **65**, 589 (1943). [d] Ref. 2.

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[1] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chap. VII.

[2] Roberts, McElhill and Armstrong, THIS JOURNAL, **71**, 2923 (1949).

[3] Kindly furnished by Dr. J. T. Clarke.

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Preparation of *d,l*-Cysteine Hydrochloride

BY RICHARD B. TURNER* AND DOROTHY M. VOITLE

Although various derivatives of *d,l*-cysteine are well known, preparation of the hydrochloride of

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* Harvard University Ph.D. 1942.